### Chapter 7

# **Quality Assurance**

#### Moheb Khalil

Environmental Bioassay Laboratory

## **Donald Padgett and Monte Steedley** *Environmental Monitoring and Analysis Group*

#### Jen Williams

ExR, Inc.

[Editor's note: The Environmental Monitoring Section (EMS) of the Savannah River Site (SRS) Environmental Protection Department (EPD) maintained the environmental quality assurance (QA) program through 2002. As part of the site's reorganization, effective the beginning of 2003, this responsibility was divided among three groups—the Environmental Monitoring Laboratory (EML), the Environmental Monitoring and Analysis group (EMA), and the Geochemical Monitoring group (GM).]

RS's environmental QA program is conducted to verify the integrity of data generated by onsite and subcontracted environmental laboratories.

The program's objectives are to ensure that samples are representative of the surrounding environment and that analytical results are accurate.

This chapter summarizes the 2003 QA program. Guidelines and applicable standards for the program are referenced in appendix A, "Applicable Guidelines, Standards, and Regulations."

Tables containing the 2003 QA data and the nonradiological detection limits can be found on the CD accompanying this report.

A more complete description of the QA program can be found in *Savannah River Site Environmental Monitoring Program* (WSRC–3Q1–2, Section 1100) and in the *Savannah River Site Environmental Monitoring Section Quality Assurance Plan* (WSRC–3Q1–2, Section 8000).

The 2003 QA data and program reviews demonstrate that the data in this annual report are reliable and meet applicable standards.

## QA for EMA Laboratories

### **Internal Quality Assurance Program**

### **Field Sampling Group**

EMA and EML personnel routinely conduct a blind sample program for field measurements of pH to assess the quality and reliability of field data measurements. EMA personnel also measure total residual chlorine, dissolved oxygen, and temperature in water samples; but because of the difficulties in providing field standards, these measurements are not suitable for a blind sample program.

During 2003, blind pH field measurements were taken for 24 samples. All field pH measurements were within the U.S. Environmental Protection Agency's (EPA's) suggested acceptable control limit of  $\pm$  0.4 pH units of the true (known) value.

#### **Chemistry and Counting Laboratories**

**Blind Tritium Samples** Blind tritium samples provide a continuous assessment of laboratory sample preparation and counting. During 2003, 12 blind samples were analyzed for tritium; all the results were within the control limits.

**Laboratory Certification** EML is certified by the South Carolina Department of Health and Environmental Control (SCDHEC) Office of Laboratory Certification for the following analytes:

- under the Clean Water Act (CWA) chemical oxygen demand, total suspended solids, field pH, total residual chlorine, temperature, and 26 metals
- under the Resource Conservation and Recovery Act (RCRA) – 50 volatile organic compounds (VOCs) and 27 metals

Table 7–1 Subcontract Laboratory Performance in ERA Water Pollution Studies

Laboratory	Water Pollution Studies (Percent Acceptable) <sup>a</sup>	
Lionville	WP 102(98%) <sup>b</sup>	
General Engineering	WP 98 (98%) <sup>c</sup>	
General Engineering Mobile Lab	WP 99 (100%)	
Shealy Environmental Services	WP 101 (94%) <sup>d</sup>	

a Laboratories are expected to exceed 80-percent-acceptable results.

- b The result for tetrachloroethane, aroclor-1260, hardness, oil and grease, alkalinity, and chloride were not acceptable.
- c Results for biological oxygen demand, chemical oxygen demand, orthophosphate (as phosphorus), and iron were not acceptable.
- d Results for copper were not acceptable.

### **External Quality Assurance Program**

In 2003, EML participated in the U.S. Department of Energy (DOE) Quality Assurance Program (QAP), an interlaboratory comparison program that tracks performance accuracy and tests the quality of environmental data reported to DOE by its contractors.

For a radiological laboratory intercomparison in 2003, the analysis of 43 isotopes was completed in March on the 58th set of QAP samples, and the analysis of four isotopes was completed in September on the 59th set. A performance rating of 95-percent acceptable was achieved on the 58th set; the rating for the 59th set was 100-percent acceptable. This rating was calculated by dividing the "acceptables" and the "acceptable with warnings" by the total number of results. Environmental QA personnel consider 80 percent to be the minimum acceptance rating in this program.

Detailed QAP intercomparison study results can be found in the data tables section of the CD accompanying this report.

### QA for Subcontracted Laboratories/EMA Laboratories

Subcontracted environmental laboratories providing analytical services must have a documented QA program and meet the quality requirements defined in the WSRC Quality Assurance Manual (WSRC 1Q).

An annual evaluation of each subcontracted laboratory is performed to ensure that all the laboratories maintain technical competence and follow the required QA programs. Each evaluation includes an examination of laboratory performance with regard to sample receipt, instrument calibration, analytical procedures,

data verification, data reports, records management, nonconformance and corrective actions, and preventive maintenance. Reports of the findings and recommendations are provided to each laboratory, and follow-up evaluations are conducted as necessary.

### Nonradiological Liquid Effluents

Effluent samples are analyzed by three onsite laboratories and two subcontracted laboratories. Laboratories must be certified by SCDHEC for all National Pollutant Discharge Elimination System (NPDES) analyses.

#### **Interlaboratory Comparison Program**

During 2003, EMA- and GM-subcontracted laboratories participated in the Environmental Resource Associates (ERA) WatR<sup>™</sup> Pollution Proficiency Testing (PT) Studies, which include various InterlaB WatR<sup>™</sup> Supply Water Pollution (WP) Performance Evaluation Programs. Performance results by the subcontracted laboratories can be found in table 7–1.

The proficiency rating is calculated as follows: acceptable parameters divided by total parameters analyzed, multiplied by 100.

EPA uses PT results to certify laboratories for specific analyses. As part of the recertification process, EPA requires that subcontracted laboratories investigate the outside-acceptance-limit results and implement corrective actions as appropriate.

Laboratories (commercial and government) that analyze NPDES samples participate in the Discharge Monitoring Report–Quality Assurance (DMR–QA) study or the WP study. Under this program, the laboratories obtain test samples from ERA. This

62 Savannah River Site

provider, as required by EPA, is accredited by the National Institute of Standards and Technology. For the 2003 DMR–QA study, Shealy Environmental Services, Inc. (SES) used the WP 101 and 102 studies; EML used the WP 100 study; and the WSRC Site Utilities Division (SUD) used the WP 101 study.

SES reported acceptable results for 16 of 17 NPDES parameters; EML reported acceptable results for 14 of 16 NPDES parameters; and the SUD Wastewater Laboratory reported acceptable results for three of three NPDES parameters.

All laboratories that participated in the DMR-QA study and experienced "not acceptable" results identified analytical problems and made corrections as necessary to pass the follow-up WP analyses and maintain SCDHE certification.

### **Intralaboratory Comparison Program**

The environmental monitoring intralaboratory program compares performance within a laboratory by analyzing duplicate and blind samples throughout the year.

SES, EML, and EMA analyzed 91 duplicate samples during 2003. Zero difference results were reported for 61of these samples.

Percent difference calculations showed that nine of the 91 duplicate samples analyzed were outside the EMA internal QA requirement (± 20 percent of the true value). None of the exceptions resulted in a difference value that was greater than the parameter detection limit. These exceptions appeared to be related to an analytical error, sample contamination, or improper sampling techniques. Generally, exceptions in this range are not considered a problem.

SES, EML, and EMA analyzed 98 blind samples during 2003. Zero difference results were reported for 66 of these samples.

Percent difference calculations showed that 11 of the 98 blind samples analyzed were outside the EMA internal QA requirement (± 20 percent of the true value). Six of the exceptions resulted in a difference value that was greater than the parameter detection limit. These exceptions appeared to be related to an analytical error, sample contamination, or improper sampling techniques. Generally, exceptions in this range are not considered a problem.

Results for the duplicate and blind sampling programs met expectations, with no indications of consistent problems in the laboratories.

### Stream and River Water Quality

SRS's water quality program requires checks of 10 percent of the samples to verify analytical results. Duplicate grab samples from SRS streams and the Savannah River were analyzed by SES and EMA in 2003. Most results were within the ± acceptance limits. Detailed stream and Savannah River water quality duplicate sample results can be found in the data tables section of the CD accompanying this report.

### Groundwater

Groundwater analyses at SRS are performed by subcontracted laboratories. SRS requires that the laboratories investigate the outside-acceptance-limit results and implement corrective actions as appropriate.

### **Internal QA**

During 2003, approximately 5 percent of the samples collected (radiological and nonradiological) for the RCRA and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) programs were submitted to the primary laboratory for analysis as blind duplicates and to a different laboratory as a QA check. The laboratories' results were evaluated on the basis of the percentage within an acceptable concentration range.

Generally, results for all QA evaluations were found to be within control limits in 2003. Full results for all QA evaluations can be obtained by contacting the EMA manager at 803–952–6931.

# External QA (Environmental Resource Associates Standards)

Quarterly Assessments During 2003, Soil and Groundwater Closure Projects (SGCP) personnel conducted quality assessments of the primary analytical laboratories to review the department's performance on certain analyses. Each laboratory received a set of certified environmental quality control standards from ERA, and its results were compared with the ERA-certified values and performance acceptance limits. The performance acceptance limits closely approximate the 95-percent confidence interval.

Results from the laboratories (EBL, General Engineering, General Engineering Mobile, Lionville, Microseeps, and Sanford Cohen and Associates) for the first three quarters are summarized in table 7–2 (fourth-quarter results not available in time for publication in this report). The results show that all the

Table 7–2 Subcontract Laboratory Performance on Environmental Resource Associates (ERA) Standards

Laboratory	1st Quarter 2003	2nd Quarter 2003	3rd Quarter 2003
EBL	96.6% <sup>a</sup>	92.4% <sup>b</sup>	92.9% <sup>c</sup>
General Engineering	98.9% <sup>d</sup>	97.5% <sup>e</sup>	97.5% <sup>f</sup>
GE Mobile Lab	100%	98.0% <sup>g</sup>	98.6% <sup>h</sup>
Lionville (Recra)	97.7% <sup>l</sup>	100%	98.9% <sup>j</sup>
Microseeps	96.9% <sup>k</sup>	94.1% <sup> </sup>	97.3% <sup>m</sup>
Sanford Cohen & Assoc.	_	55.6% <sup>n</sup>	55.6% °

- a Results for 1,1-dichloroethylene and zinc were not acceptable.
- b Results for antimony, gross alpha, mercury, nonvolatile beta, and strontium were not acceptable.
- c Results for antimony, cobalt-60, gross beta, mercury, and strontium were not acceptable.
- d Results for mercury and total phosphates (as phosphorus) were not acceptable.
- e Results for cesium-134, cobalt-60, phenols, silver, and total phosphates (as p) were not acceptable.
- f Results for cesium-134, chloride, grease & oil, silver, and turbidity were not acceptable.
- g Results for cesium-134, cyanide, and di-n-butyl phthalate were not acceptable.
- h Results for silver and tritium were not acceptable; the duplicate result for tritium was within the PAL.
- i Results for cyanide, 2,4-D, 2,4,5-T, and PCB1242 were not acceptable.
- j Results for alkalinity and bromoform were not acceptable.
- k Results for acetone, anthracene, and n-nitrosodiphenylamine/diphenylamine were not acceptable.
- I Results for acetone, arsenic, chloromethane (methyl chloride), molybdenum, styrene, and m/p-xylene were not acceptable.
- m Results for aluminum, chromium, and copper were not acceptable.
- n Results for cesium-134, cesium-137, cobalt-60, and strontium-89 were not acceptable.
- o Results for cesium-134, cobalt-60, gross beta, and strontium-89 were not acceptable.

laboratories except the Sanford Cohen facility exceeded the expected 80-percent-acceptable-results level. Sanford Cohen is not a full-service laboratory (radiological analysis only), and its performance in the 2003 DOE/QAP interlaboratory comparison program was considered acceptable. Radiological parameters were not included in the WSRC-administered QA program until 2003, and Sanford Cohen analyzed only eight radiological analytes. This made its percentage seem unacceptable when compared with the other (full service) laboratories, each of which analyzed and reported more than 200 analytes. SRS will evaluate Sanford Cohen's QA performance in January 2004 and request a corrective action plan.

### Soil/Sediment

Environmental investigations of soils and sediments, primarily for RCRA/CERCLA units, are performed by subcontracted laboratories. Data from 2003 were validated by SGCP according to EPA standards for analytical data quality, unless specified otherwise by site customers.

The environmental validation program is based on two EPA guidance documents, *Guidance for the Data* 

Quality Objectives Process for Superfund (EPA–540–R–93–071) and Data Quality Objectives Process for Hazardous Waste Sites (G–4HW) (EPA–600/R–00–007). These documents identify QA issues to be addressed, but they do not formulate a procedure for how to evaluate these inputs, nor do they propose pass/fail criteria to apply to data and documents. Hence, the validation program necessarily contains elements from—and is influenced by—several other sources, including

- Guidance on Environmental Data Verification and Data Validation (QA/G-8), EPA-240/R-02/ 004
- USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, EPA-540/R-99/008
- USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/ Furan Data Review, EPA-540/R-02/003
- USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, EPA-540/R-01/008

64 Savannah River Site

- Test Methods for Evaluating Solid Waste, EPA, November 1986, SW–846, Third Edition
- DOE Quality Systems for Analytical Services, Revision 0, July, 2003

Relative percent difference for the soil/sediment program is calculated for field duplicates and laboratory duplicates. Generally, results for all QA evaluations were found to be within control limits in 2003. A summary of this information is presented in each project report prepared by SGCP personnel.

### **Data Review**

The QA program's detailed data review for groundwater and soil/sediment analyses is described in WSRC–3Q1–2, Section 1100.

In 2003, the major QA issues discovered and addressed in connection with these programs for soil/sediment and groundwater analyses included the following:

 false positives of curium-245/246 systematically reported without qualification at one subcontract laboratory

- quantitation limits reported in place of results for detected analytes over a brief period at another subcontract laboratory
- various problems transitioning an in-house laboratory to environmental groundwater work
- data recording problems (temperature and sample association) on chains-of-custody by a sampling contractor

Items identified in 2003 that are still being addressed include the following:

- inability to demonstrate the absence of spectral interference for liquid scintillation counter radioisotopes at one subcontract laboratory
- inconsistent application of qualification policy for basic quantitation and blank contamination across all but one of the laboratories

These findings illustrate that, although laboratory procedures are well defined, analytical data quality does benefit from technical scrutiny. A corrective action plan has been put into place to address these issues, which are expected to be resolved during 2004.